

Local and global properties of mixtures in one-dimensional systems. II. Exact results for the Kirkwood–Buff integrals

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The Kirkwood–Buff integrals for two-component mixtures in one-dimensional systems are calculated directly. The results are applied to square-well particles and found to agree with those obtained by the inversion of the Kirkwood–Buff theory of solutions. © 2009 American Institute of Physics. [doi:10.1063/1.3256234]

I. INTRODUCTION

In part I of this series¹ one of us has studied both the global and the local properties of mixtures of simple particles in one-dimensional (1D) system. This work has been part of a more general advocacy in favor of the study of local properties of liquid mixtures.² Instead of the traditional study of mixtures based on the *global* properties, such as excess Gibbs energy, entropy, volume, etc., we have advocated a shift in the paradigm toward focusing on the *local* properties of the same mixtures, such as affinities between two species [embodied in the Kirkwood–Buff integrals (KBIs)], and derived quantities such as local composition, preferential solvation, and solvation thermodynamic quantities.

The local properties, though equivalent to and derivable from the global properties, offer a host of new information on the local environments of each molecular species in the mixture. This information is not conspicuous from the global properties. Therefore, the study of the local quantities offer a new and more detailed and interesting view of mixtures. In this paper we have recalculated the KBIs directly for two-component mixtures of particles interacting via square-well (SW) potential.

In Sec. II, we outline the derivation of the pair correlation functions for two-component systems in 1D system for arbitrary nearest-neighbor interactions. In Sec. III we present a sample of results for mixtures of SW particles. It is shown that the results are in quantitative agreement with those obtained in part I, which were based on the partition function method and the inversion of the Kirkwood–Buff (KB) theory of solution. We have also calculated the limiting values of the KBIs when one of the species has a vanishing mole fraction, which we could not have done from the partition function methods.

Another question examined both numerically and theoretically is the deviations from symmetrical ideal solutions and its relation with the stability of the mixtures. It is shown that no miscibility gap can occur in such mixtures.

II. THEORETICAL BACKGROUND

It is known that the correlation and thermodynamic properties of any 1D homogeneous system in equilibrium can be derived exactly, provided that every particle interacts only with its nearest neighbors.^{3–5} The aim of this section is to present a self-contained summary of the exact solution. Although the scheme extends to any number of components,⁶ here we focus on the two-component case.

A. Correlation functions

Let us consider a binary 1D fluid mixture at temperature T , pressure P , and number densities ρ_α ($\alpha=A, B$). The particles are assumed to interact only between nearest neighbors via interaction potentials $U_{\alpha\beta}(R)$. Before considering the pair correlation functions $g_{\alpha\beta}(R)$, it is convenient to introduce some probability distributions.

Given a particle of species α at a certain position, let $p_{\alpha\beta}^{(\ell)}(R)dR$ be the conditional probability of finding as its ℓ th neighbor in some direction a particle of species β at a distance between R and $R+dR$. If $\ell \geq 2$ it is obvious that the $(\ell-1)$ th neighbor of α in the same direction (being located at some point R' between 0 and R) is also a first neighbor of β . Therefore, the following recurrence condition holds:

$$p_{\alpha\beta}^{(\ell)}(R) = \sum_{\gamma=A,B} \int_0^R dR' p_{\alpha\gamma}^{(\ell-1)}(R') p_{\gamma\beta}^{(1)}(R-R'), \quad (2.1)$$

where $p_{\alpha\beta}^{(1)}(R)$ is the *nearest-neighbor* probability distribution function. On physical grounds,⁴ the ratio $p_{\alpha A}^{(1)}(R)/p_{\alpha B}^{(1)}(R)$ must become the same for $\alpha=A$ as for $\alpha=B$ in the limit of large R , i.e.,

$$\lim_{R \rightarrow \infty} \frac{p_{AA}^{(1)}(R)}{p_{AB}^{(1)}(R)} = \lim_{R \rightarrow \infty} \frac{p_{BA}^{(1)}(R)}{p_{BB}^{(1)}(R)}. \quad (2.2)$$

This relation will be used later on. The *total* probability density of finding a particle of species β , given that a particle of species α is at the origin, is

$$p_{\alpha\beta}(R) = \sum_{\ell=1}^{\infty} p_{\alpha\beta}^{(\ell)}(R). \quad (2.3)$$

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The convolution structure of Eq. (2.1) suggests the introduction of the Laplace transforms

$$\tilde{p}_{\alpha\beta}^{(\ell)}(s) = \int_0^\infty dR e^{-sR} p_{\alpha\beta}^{(\ell)}(R), \quad \tilde{p}_{\alpha\beta}(s) = \int_0^\infty dR e^{-sR} p_{\alpha\beta}(R), \quad (2.4)$$

so that Eq. (2.1) becomes

$$\tilde{p}_{\alpha\beta}^{(\ell)}(s) = \sum_{\gamma=A,B} \tilde{p}_{\alpha\gamma}^{(\ell-1)}(s) \tilde{p}_{\gamma\beta}^{(1)}(s). \quad (2.5)$$

Equation (2.5) allows us to express $\tilde{p}_{\alpha\beta}^{(\ell)}(s)$ in terms of the nearest-neighbor distribution as

$$\tilde{\mathbf{p}}^{(\ell)}(s) = [\tilde{\mathbf{p}}^{(1)}(s)]^\ell, \quad (2.6)$$

where $\tilde{\mathbf{p}}^{(\ell)}(s)$ is the 2×2 matrix of elements $\tilde{p}_{\alpha\beta}^{(\ell)}(s)$. From Eqs. (2.3) and (2.6) we get

$$\tilde{\mathbf{p}}(s) = \sum_{\ell=1}^{\infty} [\tilde{\mathbf{p}}^{(1)}(s)]^\ell = \tilde{\mathbf{p}}^{(1)}(s) \cdot [\mathbf{1} - \tilde{\mathbf{p}}^{(1)}(s)]^{-1}, \quad (2.7)$$

where $\tilde{\mathbf{p}}(s)$ is the 2×2 matrix of elements $\tilde{p}_{\alpha\beta}(s)$ and $\mathbf{1}$ is the 2×2 unity matrix.

Now, notice that the pair correlation function $g_{\alpha\beta}(R)$ and the probability density $p_{\alpha\beta}(R)$ are simply related by $p_{\alpha\beta}(R) = \rho_\beta g_{\alpha\beta}(R)$ or, equivalently in Laplace space,

$$\tilde{p}_{\alpha\beta}(s) = \rho_\beta \tilde{g}_{\alpha\beta}(s), \quad (2.8)$$

where

$$\tilde{g}_{\alpha\beta}(s) = \int_0^\infty dR e^{-sR} g_{\alpha\beta}(R), \quad (2.9)$$

is the Laplace transform of $g_{\alpha\beta}(R)$. Therefore, thanks to the 1D nature of the model and the restriction to nearest-neighbor interactions, the knowledge of the nearest-neighbor distributions $p_{\alpha\beta}^{(1)}(R)$ suffices to obtain the pair correlation functions $g_{\alpha\beta}(R)$. More explicitly, from Eqs. (2.7) and (2.8) the Laplace transforms $\tilde{g}_{\alpha\beta}(s)$ are found to be

$$\tilde{g}_{AA}(s) = \frac{1}{\rho_T} \frac{Q_{AA}(s)[1 - Q_{BB}(s)] + Q_{AB}^2(s)}{x_A D(s)}, \quad (2.10)$$

$$\tilde{g}_{BB}(s) = \frac{1}{\rho_T} \frac{Q_{BB}(s)[1 - Q_{AA}(s)] + Q_{AB}^2(s)}{x_B D(s)}, \quad (2.11)$$

$$\tilde{g}_{AB}(s) = \frac{1}{\rho_T} \frac{Q_{AB}(s)}{\sqrt{x_A x_B} D(s)}, \quad (2.12)$$

where $\rho_T = \rho_A + \rho_B$ is the total number density, $x_\alpha = \rho_\alpha / \rho_T$ is the mole fraction of species α , and we have called

$$Q_{\alpha\beta}(s) \equiv \sqrt{\frac{x_\alpha}{x_\beta}} \tilde{p}_{\alpha\beta}^{(1)}(s), \quad (2.13)$$

$$D(s) \equiv [1 - Q_{AA}(s)][1 - Q_{BB}(s)] - Q_{AB}^2(s). \quad (2.14)$$

The KBIs in the 1D case are defined by

$$G_{\alpha\beta} = 2 \int_0^\infty dR [g_{\alpha\beta}(R) - 1]. \quad (2.15)$$

In terms of the Laplace transform $\tilde{g}_{\alpha\beta}(s)$, Eq. (2.15) can be rewritten as

$$G_{\alpha\beta} = 2 \lim_{s \rightarrow 0} \left[\tilde{g}_{\alpha\beta}(s) - \frac{1}{s} \right]. \quad (2.16)$$

We see that only the nearest-neighbor distribution $p_{\alpha\beta}^{(1)}(R)$ is needed to close the problem. It can be proven^{4,5} that $p_{\alpha\beta}^{(1)}(R)$ is just proportional to the Boltzmann factor $e^{-U_{\alpha\beta}(R)/k_B T}$ times a decaying exponential $e^{-\xi R}$, where the damping coefficient is $\xi = P/k_B T$. Therefore,

$$p_{\alpha\beta}^{(1)}(R) = x_\beta K_{\alpha\beta} e^{-U_{\alpha\beta}(R)/k_B T} e^{-\xi R}, \quad (2.17)$$

where the proportionality constants $K_{\alpha\beta} = K_{\beta\alpha}$ (which of course depend on the thermodynamic state of the mixture) will be determined below by applying physical consistency conditions. Taking Laplace transforms in Eq. (2.17) and inserting the result into Eq. (2.13) we get

$$Q_{\alpha\beta}(s) = \sqrt{x_\alpha x_\beta} K_{\alpha\beta} \Omega_{\alpha\beta}(s + \xi), \quad (2.18)$$

where

$$\Omega_{\alpha\beta}(s) = \int_0^\infty dR e^{-sR} e^{-U_{\alpha\beta}(R)/k_B T}, \quad (2.19)$$

is the Laplace transform of $e^{-U_{\alpha\beta}(R)/k_B T}$.

To recapitulate, given the interaction potentials $U_{\alpha\beta}(R)$ and given a particular thermodynamic state (P, T, x_A) , the three correlation functions are obtained (in Laplace space) from Eqs. (2.10)–(2.12), supplemented by Eqs. (2.14), (2.18), and (2.19).

B. Equation of state

In order to close the exact solution, it only remains to determine the total density ρ_T (equation of state) and the amplitudes $K_{\alpha\beta}$ as functions of P , T , and $x_A = 1 - x_B$. As said above, they can be easily obtained by applying basic physical conditions. First, note that Eq. (2.2) establishes the following relationship:

$$K_{AB}^2 = K_{AA} K_{BB}. \quad (2.20)$$

Next, the physical condition $\lim_{R \rightarrow \infty} g_{\alpha\beta}(R) = 1$ implies that $\tilde{g}_{\alpha\beta}(s) \rightarrow 1/s$ for small s . According to Eqs. (2.10)–(2.12), this is only possible if $D(0) = 0$, so that $D(s) \rightarrow D'(0)s$ for small s , where $D'(s) = dD(s)/ds$. Thus, one has

$$[1 - Q_{AA}(0)][1 - Q_{BB}(0)] - Q_{AB}^2(0) = 0, \quad (2.21)$$

$$\rho_T = \frac{Q_{AB}(0)}{\sqrt{x_A x_B} D'(0)}, \quad (2.22)$$

$$\rho_T = \frac{Q_{AA}(0)[1 - Q_{BB}(0)] + Q_{AB}^2(0)}{x_A D'(0)}, \quad (2.23)$$

$$\rho_T = \frac{Q_{BB}(0)[1 - Q_{AA}(0)] + Q_{AB}^2(0)}{x_B D'(0)}. \quad (2.24)$$

Elimination of ρ_T between Eqs. (2.22)–(2.24) yields two coupled equations which, together with Eq. (2.21), gives

$$K_{AA} = \frac{1 - x_B K_{AB} \Omega_{AB}(\xi)}{x_A \Omega_{AA}(\xi)}, \quad (2.25)$$

$$K_{BB} = \frac{1 - x_A K_{AB} \Omega_{AB}(\xi)}{x_B \Omega_{BB}(\xi)}. \quad (2.26)$$

Insertion of Eqs. (2.25) and (2.26) into Eq. (2.20) allows one to obtain a quadratic equation for K_{AB} whose physical root is

$$K_{AB} = \frac{1}{\Omega_{AB}(\xi)} \frac{1 - \sqrt{1 - 4x_A x_B (1 - R)}}{2x_A x_B (1 - R)}, \quad (2.27)$$

where we have called

$$R \equiv \frac{\Omega_{AA}(\xi)\Omega_{BB}(\xi)}{\Omega_{AB}^2(\xi)}. \quad (2.28)$$

It is interesting to note that, since $K_{\alpha\beta}$ and $\Omega_{\alpha\beta}$ are positive definite, Eq. (2.25) and (2.26) imply that $x_\alpha K_{AB} \Omega_{AB}(\xi) < 1$ for $\alpha = A, B$, i.e.,

$$K_{AB} \Omega_{AB}(\xi) < \min\left(\frac{1}{x_A}, \frac{1}{x_B}\right) \leq 2. \quad (2.29)$$

Finally, the density ρ_T is obtained from either of Eqs. (2.22)–(2.24). The result is

$$\rho_T(P, T, x_A) = - \frac{1}{x_A^2 K_{AA} \Omega'_{AA}(\xi) + x_B^2 K_{BB} \Omega'_{BB}(\xi) + 2x_A x_B K_{AB} \Omega'_{AB}(\xi)}, \quad (2.30)$$

where $\Omega'_{\alpha\beta}(s)$ is the first derivative of $\Omega_{\alpha\beta}(s)$.

Equations (2.25)–(2.28) and (2.30) complete the full determination of $\tilde{g}_{\alpha\beta}(s)$ and the equation of state for any choice of the nearest-neighbor interaction potentials $U_{\alpha\beta}(x)$ and of the thermodynamic state (P, T, x_A) .

C. Kirkwood–Buff integrals

The KBI $G_{\alpha\beta}$ can be derived, according to Eq. (2.16), by expanding $s\tilde{g}_{\alpha\beta}(s)$ in powers of s as $s\tilde{g}_{\alpha\beta}(s) = 1 + \frac{1}{2}G_{\alpha\beta}s + \dots$ and identifying the linear term. After some algebra one gets

$$G_{AB} = \rho_T J + 2 \frac{\Omega'_{AB}(\xi)}{\Omega_{AB}(\xi)}, \quad (2.31)$$

$$G_{AA} = \rho_T J - 2 \frac{x_B K_{BB} \Omega'_{BB}(\xi)}{x_A K_{AB} \Omega_{AB}(\xi)} - \frac{2}{\rho_T x_A}, \quad (2.32)$$

$$G_{BB} = \rho_T J - 2 \frac{x_A K_{AA} \Omega'_{AA}(\xi)}{x_B K_{AB} \Omega_{AB}(\xi)} - \frac{2}{\rho_T x_B}, \quad (2.33)$$

where

$$J \equiv x_A^2 K_{AA} \Omega''_{AA}(\xi) + x_B^2 K_{BB} \Omega''_{BB}(\xi) + 2x_A x_B K_{AB} \Omega''_{AB}(\xi) - 2x_A x_B K_{AB} \frac{\Omega'_{AA}(\xi)\Omega'_{BB}(\xi) - [\Omega'_{AB}(\xi)]^2}{\Omega_{AB}(\xi)}. \quad (2.34)$$

The knowledge of the KBIs allows us to obtain the (reduced) isothermal compressibility

$$\chi = k_B T \left(\frac{\partial \rho_T}{\partial P} \right)_{T, x_A}, \quad (2.35)$$

by means of

$$\chi = \frac{1 + \rho_T (x_A G_{AA} + x_B G_{BB}) + \rho_T^2 x_A x_B (G_{AA} G_{BB} - G_{AB}^2)}{1 + \rho_T x_A x_B \Delta_{AB}}, \quad (2.36)$$

where

$$\Delta_{AB} \equiv G_{AA} + G_{BB} - 2G_{AB}. \quad (2.37)$$

It can be checked that the resulting expression of χ (which, due to its length, will be omitted here) coincides with the one obtained as $\chi = (\partial \rho_T / \partial \xi)_{T, x_A}$ from Eq. (2.30). This confirms the exact character of the solution.

Making use of Eqs. (2.30)–(2.33), it is easy to prove that

$$1 + \rho_T x_A x_B \Delta_{AB} = \frac{2}{K_{AB} \Omega_{AB}(\xi)} - 1, \quad (2.38)$$

which according to Eq. (2.29) is a positive definite quantity. More explicitly, from Eq. (2.27) we have

$$1 + \rho_T x_A x_B \Delta_{AB} = \sqrt{1 - 4x_A x_B (1 - R)}. \quad (2.39)$$

Therefore, the denominator in Eq. (2.36) never vanishes and the isothermal compressibility is well defined. This agrees with van Hove's classical proof⁷ that no phase transition can exist in this class of nearest-neighbor 1D models.

Let us now obtain the KBIs in the infinite dilution limit $x_A \rightarrow 0$. In that limit, Eqs. (2.25)–(2.27) and (2.30) become

$$K_{AA} = \frac{\Omega_{BB}(\xi)}{\Omega_{AB}^2(\xi)}, \quad K_{BB} = \frac{1}{\Omega_{BB}(\xi)}, \quad K_{AB} = \frac{1}{\Omega_{AB}(\xi)}, \quad (2.40)$$

$$\rho_T = - \frac{\Omega_{BB}(\xi)}{\Omega'_{BB}(\xi)}. \quad (2.41)$$

Analogously, from Eqs. (2.31)–(2.34) one gets

$$G_{AB} = - \frac{\Omega''_{BB}(\xi)}{\Omega'_{BB}(\xi)} + 2 \frac{\Omega'_{AB}(\xi)}{\Omega_{AB}(\xi)}, \quad (2.42)$$

$$G_{AA} = - \frac{\Omega''_{BB}(\xi)}{\Omega'_{BB}(\xi)} + 4 \frac{\Omega'_{AB}(\xi)}{\Omega_{AB}(\xi)} - 2 \frac{\Omega_{AA}(\xi)\Omega'_{BB}(\xi)}{\Omega_{AB}^2(\xi)}, \quad (2.43)$$

$$G_{BB} = - \frac{\Omega''_{BB}(\xi)}{\Omega'_{BB}(\xi)} + 2 \frac{\Omega'_{BB}(\xi)}{\Omega_{BB}(\xi)}, \quad (2.44)$$

$$\Delta_{AB} = 2\Omega'_{BB}(\xi) \left[\frac{1}{\Omega_{BB}(\xi)} - \frac{\Omega_{AA}(\xi)}{\Omega_{AB}(\xi)} \right]. \quad (2.45)$$

Note that special care is needed to obtain K_{AA} and G_{AA} .

D. Chemical potentials and solvation Gibbs energies

Finally, let us get an explicit expression for the chemical potential. From the KB theory of solution we have^{2,8}

$$\begin{aligned} \frac{1}{k_B T} \left(\frac{\partial \mu_A}{\partial x_A} \right)_{P,T} &= \frac{1}{x_A} - \frac{\rho_T x_A \Delta_{AB}}{1 + \rho_T x_A x_B \Delta_{AB}} \\ &= \frac{1}{x_A} - \frac{1}{x_B} \frac{\sqrt{1 - 4x_A x_B (1-R)} - 1}{\sqrt{1 - 4x_A x_B (1-R)}}, \end{aligned} \quad (2.46)$$

where in the last step we have made use of Eq. (2.39). Integration over x_A yields

$$\begin{aligned} \frac{\mu_A}{k_B T} &= \text{const} + \ln x_A + \ln[1 - 2x_B(1-R) \\ &\quad + \sqrt{1 - 4x_A x_B (1-R)}]. \end{aligned} \quad (2.47)$$

For pure A ($x_B=0$), we have

$$\frac{\mu_A^P}{k_B T} = \text{const} + \ln 2. \quad (2.48)$$

The solvation Gibbs energy of A in pure A may be obtained from Eq. (2.47) as^{2,9}

$$\Delta \mu_A^* = \mu_A - k_B T \ln(\rho_A \Lambda_A), \quad (2.49)$$

where $\Lambda_A = h / \sqrt{2\pi m_A k_B T}$ is the momentum partition function of A in 1D systems. Similarly,

$$\Delta \mu_A^{*P} = \mu_A^P - k_B T \ln(\rho_A^P \Lambda_A), \quad (2.50)$$

where ρ_A^P is the density of pure A at the same T and P as the mixture. Taking the limit $x_B \rightarrow 0$ in Eqs. (2.25) and (2.30) one has

$$\rho_A^P = - \frac{\Omega_{AA}(\xi)}{\Omega'_{AA}(\xi)}. \quad (2.51)$$

The excess solvation Gibbs energy relative to the solvation Gibbs energy in pure A is defined as

$$\Delta \Delta \mu_A^* = \Delta \mu_A^* - \Delta \mu_A^{*P}. \quad (2.52)$$

This quantity may be calculated from Eqs. (2.47)–(2.52) with the result

$$\begin{aligned} \frac{\Delta \Delta \mu_A^*}{k_B T} &= \ln \left[\frac{1}{2} - x_B(1-R) + \frac{1}{2} \sqrt{1 - 4x_A x_B (1-R)} \right] \\ &\quad + \ln \frac{\rho_A^P}{\rho_T}. \end{aligned} \quad (2.53)$$

III. A SAMPLE OF RESULTS

Let us start considering a binary system composed of (additive) hard rods of different diameters (lengths) σ_{AA} , σ_{BB} , and $\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2$. The Laplace function $\Omega_{\alpha\beta}(s)$ defined by Eq. (2.19) is

$$\Omega_{\alpha\beta}(s) = \frac{e^{-s\sigma_{\alpha\beta}}}{s}. \quad (3.1)$$

In this case the parameter defined in Eq. (2.28) is $R=1$ and thus the limit $R \rightarrow 1$ must be taken in Eq. (2.27) with the

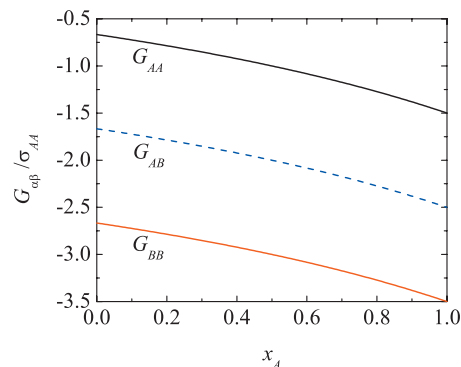


FIG. 1. The KBIs $G_{\alpha\beta}$ for hard rods of different diameters $\sigma_{BB}/\sigma_{AA}=2$ and $P\sigma_{AA}/k_B T=1$.

result $K_{AB}=1/\Omega_{AB}(\xi)$. The general scheme of Sec. II can be used to obtain the KBIs explicitly

$$G_{AB} = - \frac{\sigma_{AA} + \sigma_{BB} + \xi \sigma_{AA} \sigma_{BB}}{1 + \xi(x_A \sigma_{AA} + x_B \sigma_{BB})}, \quad (3.2)$$

$$G_{AA} = G_{AB} + \sigma_{BB} - \sigma_{AA}, \quad (3.3)$$

$$G_{BB} = G_{AB} + \sigma_{AA} - \sigma_{BB}, \quad (3.4)$$

so that $\Delta_{AB}=0$. Figure 1 shows the values of $G_{\alpha\beta}$ for a diameter ratio $\sigma_{BB}/\sigma_{AA}=2$ and a thermodynamic state $P\sigma_{AA}/k_B T=1$. These results are in perfect agreement with those calculated in part I.¹

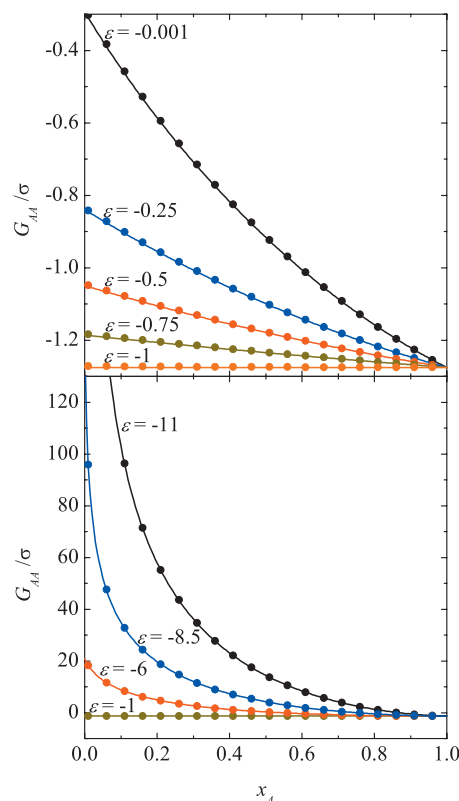


FIG. 2. The KBI G_{AA} for SW particles with parameters given in Eq. (3.7) and $k_B T/|\epsilon_{AA}|=1$, $P\sigma/k_B T=1$. The lines are obtained from the exact expressions presented in Sec. II C, while the circles are the data obtained in Ref. 1.

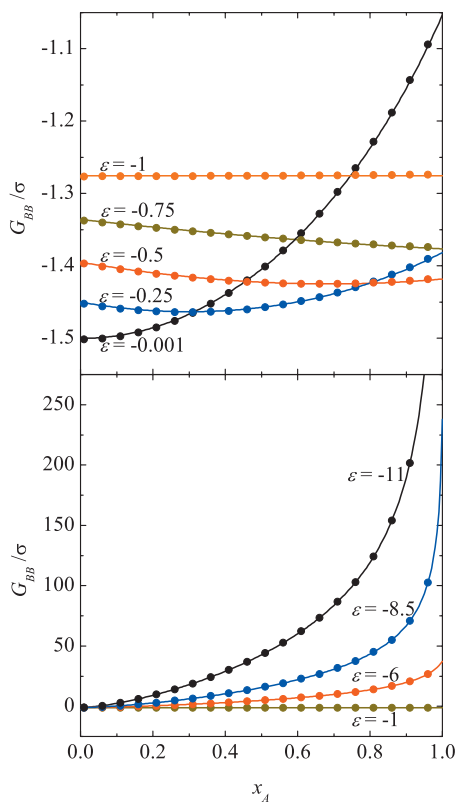


FIG. 3. The KBI G_{BB} for SW particles with parameters given in Eq. (3.7) and $k_B T/|\epsilon_{AA}|=1$, $P\sigma/k_B T=1$. The lines are obtained from the exact expressions presented in Sec. II C, while the circles are the data obtained in Ref. 1.

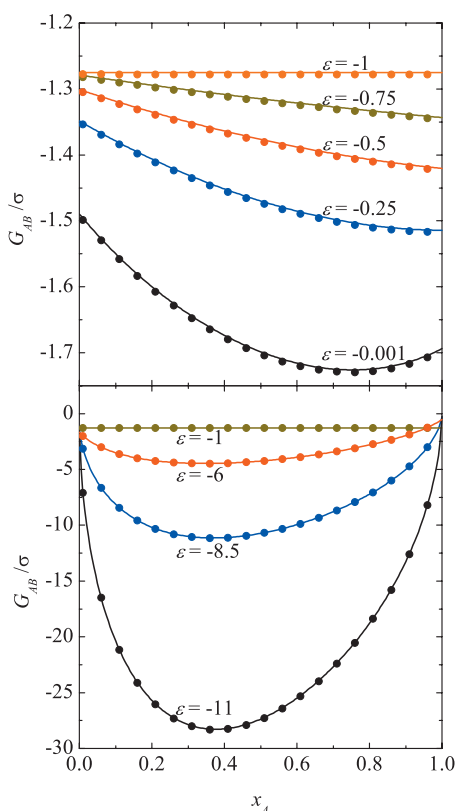


FIG. 4. The KBI G_{AB} for SW particles with parameters given in Eq. (3.7) and $k_B T/|\epsilon_{AA}|=1$, $P\sigma/k_B T=1$. The lines are obtained from the exact expressions presented in Sec. II C, while the circles are the data obtained in Ref. 1.

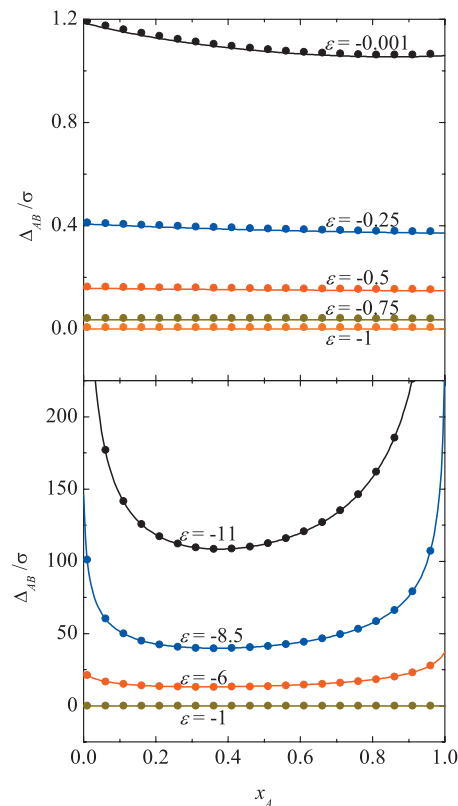


FIG. 5. Values of Δ_{AB} for SW particles with parameters given in Eq. (3.7) and $k_B T/|\epsilon_{AA}|=1$, $P\sigma/k_B T=1$. The lines are obtained from the exact expressions presented in Sec. II C, while the circles are the data obtained in Ref. 1.

Having established that the programs give the correct results for hard rods, we next present results for a mixture of particles' interaction via SW potential of the form

$$U_{\alpha\beta}(R) = \begin{cases} \infty, & R < \sigma_{\alpha\beta} \\ \epsilon_{\alpha\beta}, & \sigma_{\alpha\beta} < R < \sigma_{\alpha\beta} + \delta_{\alpha\beta} \\ 0, & R < \sigma_{\alpha\beta} + \delta_{\alpha\beta}, \end{cases} \quad (3.5)$$

where $\epsilon_{\alpha\beta} < 0$. For this SW potential the Laplace function $\Omega_{\alpha\beta}(s)$ is

$$\Omega_{\alpha\beta}(s) = \frac{e^{-s\sigma_{\alpha\beta}}}{s} [e^{-\epsilon_{\alpha\beta}/k_B T} - (e^{-\epsilon_{\alpha\beta}/k_B T} - 1)e^{-s\delta_{\alpha\beta}}], \quad (3.6)$$

and again the general results of Sec. II provide the KBIs explicitly.

We have taken the following values for the potential parameters:

$$\begin{aligned} \sigma_{AA} &= \sigma_{BB} = \sigma_{AB} = \sigma, \\ \delta_{AA} &= \delta_{BB} = \delta_{AB} = \frac{1}{5}\sigma, \end{aligned} \quad (3.7)$$

$$\frac{\epsilon_{BB}}{|\epsilon_{AA}|} = \epsilon, \quad \epsilon_{AB} = -\sqrt{\epsilon_{AA}\epsilon_{BB}}.$$

The thermodynamic variables are T , P , and x_A . In all the calculations we choose $k_B T/|\epsilon_{AA}|=1$ and $P\sigma/k_B T=1$ to compare the present results with those of part I.

Figures 2–4 show the values of G_{AA} , G_{BB} , and G_{AB} for

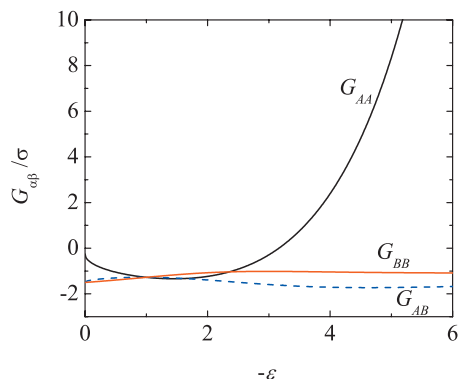


FIG. 6. The KBI $G_{\alpha\beta}$ in the infinite dilution limit ($x_A \rightarrow 0$) for SW particles with parameters given in Eq. (3.7) and $k_B T/|\epsilon_{AA}|=1$, $P\sigma/k_B T=1$.

these systems for various values of ϵ ranging from $\epsilon = -0.001$ to $\epsilon = -1$, and from $\epsilon = -1$ to $\epsilon = -11$.¹⁰ Figure 5 shows the values of $\Delta_{AB} = G_{AA} + G_{BB} - 2G_{AB}$ in the entire range of composition. In all the cases the agreement with the results of part I is quantitative.

The KBIs in the infinite dilution limit ($x_A \rightarrow 0$), as obtained from Eqs. (2.42)–(2.44), are plotted in Fig. 6 as functions of $-\epsilon$ for the same system as that of Figs. 2–5. We observe that both G_{AB} and G_{BB} are hardly sensitive to the value of ϵ . In contrast, the solute-solute KBI, G_{AA} , is strongly influenced by the solvent-solvent potential depth, increasing both for small and for large values of $|\epsilon|$. A careful inspection of the explicit expressions (2.42)–(2.44) in the limit $|\epsilon| \rightarrow \infty$ shows that, while G_{AB} and G_{BB} tend to the same constant value, G_{AA} diverges as $G_{AA} \sim \exp[(|\epsilon_{BB}| - 2|\epsilon_{AB}|)/k_B T]$. This phenomenon might be relevant to the study of hydrophobic interactions, as discussed in Ref. 9.

IV. DISCUSSION AND CONCLUSION

In part I we calculated all the KBIs in an indirect way.¹ We first calculated the excess functions from the partition function of the system, then we used the inversion of the KB theory² to calculate the KBIs. This lengthy procedure might have introduced accumulated errors. Some readers of part I have expressed doubts regarding the reliability of the results calculated along this procedure. In fact some have also claimed that there might be a miscibility gap, which we

might have missed by this indirect and lengthy calculations. In this paper we have repeated the calculations of the KBIs directly from the same program that was designed to calculate the pair correlation functions in mixtures of two components in 1D system.

The agreement between the two methods was satisfying, it also lent credibility to the inversion procedure and encouraged us to extend the calculations of the KBIs for aqueous-like mixtures.⁹ We hope to report on that in the near future.

Regarding the question of miscibility gap we have shown that the inequality

$$1 + \rho_T x_A x_B \Delta_{AB} > 0, \quad (4.1)$$

always holds in these mixtures, as shown by Eq. (2.39).

From the KB theory^{2,8} of solution we have the equation

$$\left(\frac{\partial^2 g}{\partial x_A^2}\right)_{P,T} = \frac{1}{x_B} \left(\frac{\partial \mu_A}{\partial x_A}\right)_{P,T} = \frac{k_B T}{x_A x_B (1 + \rho_T x_A x_B \Delta_{AB})}, \quad (4.2)$$

where $g = G/(N_A + N_B)$ is the Gibbs energy of the system per mole of mixture. It follows from Eqs. (4.1) and (4.2) that g is everywhere a concave (downward) function of x_A . Therefore, there exists no region of compositions where the system is not stable, hence no phase transition in such a system.

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